HIGHLY ORIENTED MESOPHASE PITCH-BASED GRAPHITE TAPE AND BULK CARBON MATERIAL

The present invention relates to a method for producing highly oriented mesophase pitch-based tapes and to a method for producing highly oriented bulk carbon materials from the highly oriented mesophase pitch-based tapes, and to the tapes and the bulk carbon materials *per se* and to composite materials that contain continuous or discontinuous tapes.

The graphite crystal is rendered highly anisotropic by its structure which is composed of stacks of sheet-like layers of carbon atoms (graphene layers). In the plane of the sheets, the carbon atoms are covalently bonded by sp^2 hybridisation of the electron orbitals. These layer planes are weakly held together by weak Van Der Waals-type forces. Theoretically graphite has exceptionally high elastic modulus (1060GPa) and it also displays extremely high thermal conductivity along the basal plane (significantly higher than that of most conductive metals such as copper and silver, even higher in specific terms). It follows that in an article made of perfectly aligned graphene planes, the material would have extremely high tensile elastic modulus in the basal plane directions since the load would be opposed by the covalent bonds themselves.

There are no artificial bulk carbon and graphite materials available with properties equivalent to those of the graphite crystal. However, there are carbon and graphite materials which have realised a fraction of these properties. An extremely wide range of properties may be engineered in carbon materials which may be produced from a variety of precursors through different processing routes.

Carbon materials are widely used and play an essential role in aerospace, nuclear, metallurgical, chemical, mechanical and electrical applications.

Bulk carbon and graphite materials (such as electrodes used for steel making and anodes for the aluminium industry) are produced from carbonaceous filler particles (cokes, graphite or carbon black) combined with a pitch binder. The raw materials are mixed to ensure even distribution of the binder and then formed by extrusion or moulding. The bulk product is calcined and the pitch binder decomposes to carbon. A high temperature of >2500°C is required to convert the carbon to graphite. At this stage the graphite bulk density is of the order of ~1.7 Mgm^{-3} with a porosity in the region of ~25%. Thus the fabrication process usually requires lengthy, multiple pitch impregnation and pyrolysis cycles to reduce the porosity.

The properties of the filler coke particles and pitch binder as well as the processing conditions strongly influence the properties of the final bulk graphite artefacts. Coke particles may show preferred orientation along the extrusion direction which is particularly true if anisotropic or "needle" cokes are used giving an electrode with anisotropic properties. The properties of carbon and graphite materials produced in this way are complicated by the anisotropic nature of the crystallites but (generally speaking) they are porous and of low strength. The bulk anisotropic properties are dependent on the size and arrangement of crystallites within the structure.

The cokes used in this process are often produced from petroleum pitches. During pyrolysis most pitches pass

through a discotic nematic liquid crystal phase when the polyaromatic molecules align in domains. This is an essential stage in the formation of graphitising carbon from such precursors. It is known as the carbonaceous mesophase and has been exploited to produce advanced carbon and graphite fibres and composites.

Carbonaceous mesophase may be formed in complex polycyclic aromatic hydrocarbon mixtures such as petroleum or coal tar pitches when heated within the temperature range 350-500°C [Brooks et al (1965). Carbon 3, p 185]. In the early stages of the transformation, mesophase precipitates from the pyrolysing matrix as small spheres. According to the Brooks-Taylor model, within the central region the mesophase layers lie parallel to define the polar diameter but curve to meet the interface with the pitch matrix at a high angle. As pyrolysis proceeds, these mesophase spheres grow and coalesce to larger spheres. Coalesced mesophase spheres show more complicated extinction patterns than the spheres which first appear (see Figure 1). As pyrolysis continues, the coalescence proceeds and eventually the material becomes entirely or substantially converted to the mesophase state.

Certain mesophase pitches can be formed into fibres through melt spinning. The mesophase pitch melt is usually extruded through a multiple-hole spinneret. The extrudates are draw down as they cool and eventually solidify to form the fibres. When molten mesophase pitch is forced through the spinneret, the planar polyaromatic molecules are lined up in the flow direction. The alignment is further improved during the fibre drawdown. Hence, the polyaromatic molecules are aligned more or less parallel to the fibre axis in the "as-spun" fibres and thereby producing fibres with

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exceptional stiffness after carbonisation and
graphitisation. For a given pitch, the spinning conditions
have a strong impact on the degree of preferred orientation
of "as-spun" fibres which is higher when the spinning
viscosity is low. It has been suggested that mesophase
pitch-based fibres of larger diameter produced from lower
viscosity precursors have a higher degree of preferred
orientation. The fibres of smaller diameter cool more
rapidly during the elongation process thereby inheriting a
lower degree of preferred orientation as disordered states
at higher temperature are locked in.

In order to retain the fibre shape and the preferred
orientation of mesophase molecules induced during spinning,
"as-spun" fibres must be stabilised to render them infusible
before further heat treatment. Stabilisation is normally
achieved through oxidation in which the "as-spun" fibres are
heated in an oxygen-containing atmosphere to temperatures
between 200 and 350°C for a period of time sufficient to
prevent fibres deforming and/or sticking during
carbonisation. The stabilisation step can have a
significant impact on the microstructure as well as the
mechanical strength of the finished fibres. Two kinds of
chemical reactions take place simultaneously during
stabilisation. The first is oxygen uptake into the fibre
constituents and the second is the evolution of volatile
organic vapours and oxygen-containing gases. The weight gain
is rapid in the early stages of oxidation but decreases with
prolonged exposure. The amount of oxygen uptake is critical.
It must be adequate to preclude interfusion of fibres yet
low enough not to disrupt the fibre structure when it is
eventually expelled as CO and CO_2 during carbonisation. An
oxygen uptake of 6 to 7 wt% is known to be adequate for

stabilisation. The oxygen absorbed by the fibre forms oxygen-containing functional groups that may cross-link and preserve the axial preferred orientation of the fibre during carbonisation and reduce the solubility of the fibre constituents.

Stabilised pitch fibres are infusible. They have poor mechanical properties, are fragile and difficult to handle. Carbonisation of the stabilised fibres is required to convert the molecular solid into a paracrystalline carbon state. Graphitisation at temperatures above 2000°C is a further option and is known to confer exceptional properties. Graphitisation involves the development of graphitic order in the fibres. The highly oriented structure of the "as-spun" fibres is enhanced in the carbonised state provided that they have been sufficiently well oxidised prior to carbonisation. Increasing the final heat treatment temperature brings about an increase in crystallite size and perfection and in the degree of preferred orientation of layer planes along the fibre axis thereby resulting in an improvement in mechanical and other properties.

The mechanical properties of pitch-based carbon fibres produced by BP-Amoco are listed in Table 1 [BP-Amoco data sheet]. In the extreme cases, these mesophase pitch-based carbon fibres may display a high modulus which is very close to the theoretical value of single crystalline graphite.

Table 1. Properties of some highly oriented BP-Amoco pitch-based carbon fibres

Fibres	Diameter μm	Tensile strength GPa	Young's modulus GPa	Elongation to failure %	Density Mgm^{-3}	Thermal Conductivity Wm^{-1}k^{-1}
P120s	10	2.41	827	0.3	2.17	640
K1100	10	3.10	965	-	2.20	900-1000

Carbon fibres may have excellent mechanical and transport properties but only in one direction. For effective use in composites they are combined in woven structures to give two, three and multi-directional properties. The formation of complete woven structures is an additional cost in the production of high performance composites.

The need for materials capable of withstanding the tremendous thermal erosion and thermal shock experienced by spacecraft and rockets has led directly to the development of carbon-carbon composites. A carbon-carbon composite is a carbon fibre-reinforced carbon matrix material. Carbon fibres are produced from a variety of precursors including pitch, polyacrylonitrile (PAN), rayon and organic vapours. The carbon matrix phase is typically formed by solid, liquid, or gaseous-phase pyrolysis of an organic precursor material. Carbon-carbon composites seek to combine the high strength, stiffness and toughness of carbon fibre with the excellent thermomechanical properties of bulk polygranular carbons. There are two main methods of formation of the carbon matrix, namely (1) chemical vapour deposition from a hydrocarbon gas (CVD) or (2) carbonisation of a carbonaceous resin or pitch.

The variety of structures displayed by carbon fibres and carbon matrices give the composite a broad range of

properties (mechanical and physical). In addition, the
interaction between the carbon fibres and the matrix carbons
plays an important role in determining the properties of the
composite. Properties of carbon-carbon composites that make
them attractive substitutes for other structural materials
(such as metals and alloys) include high specific strength
and stiffness, high temperature strength, high corrosion
resistance, low thermal expansion, good friction and wear
properties and high thermal and electrical conductivity. The
use of these high performance materials has been developed
in areas as diverse as integrated rocket throat nozzles,
nosecones, aircraft brakes, structural materials in the
aerospace industry, molten glass handling and biomedical
implants.

The very high thermal conductivity of mesophase pitch-based
carbon fibres is due to a highly oriented graphite
crystalline structure along the fibre axis. The thermal
conductivity of the mesophase pitch-based carbon fibre
Thornel K-1100 is 900-1000$Wm^{-1}K^{-1}$ which is more than twice
that of copper or 10 times in specific terms. One high
profile application of mesophase pitch-based carbon fibre
reinforced composites is their use as thermal management
materials such as satellite radiators and electronic
packagings. Perceived new widespread applications such as
heat sinks leads to a need for improved materials and new
production methods.

As mentioned hereinbefore, the low mechanical and poor
transport properties of polygranular materials are
attributable to the high porosity and almost random
orientation of the crystallites. An approach that reduces
porosity is the method of producing so-called "sintered"

carbons, although the random orientation of crystallites
still pervades.

Sintered carbons can be made by grinding a mesophase pitch
into particles, forming the ground particles into desired
shape and finally heating the shaped article to carbonise
it. This ground mesophase has to be stabilised to a certain
degree or otherwise treated to control its thermoplasticity;
too little thermoplasticity and the powder becomes
undeformable and yields low green densities, too much
thermoplasticity and the powder becomes too fluid and
'bloats'. The intrinsic density of the powder increases
progressively with heat treatment through to graphitisation
temperatures. The particle shrinkage is due to the decrease
in its inter-basal plane spacing (d_{002}) which approaches that
of graphite crystal. Thus to produce high-density, high
strength carbons the shrinkage of the bulk material must be
matched by the shrinkage of the particles to avoid the
formation of pores. Although high strength high-density bulk
materials can be produced, they still have isotropic
properties due to a lack of preferred orientation of the
crystallites.

Similar to the production of sintered carbon, highly
oriented bulk carbon materials can be produced by pressing
mesophase pitch-based fibres. This has been adopted in the
so-called self-reinforcing method by pressing the as-spun
mesophase pitch fibres into panels before thermosetting and
further heat treatment [Barr et al, 22th Biennial Conf. on
Carbon, 1995, p.32]. BP-Amoco Performance Products Inc.
recently developed a family of self-reinforced panels
(ThermalGraph[R]) from as-spun mesophase pitch fibres (average
diameter ~10μm). The high thermal conductivity of mesophase

pitch-based carbon fibres is attributable to the extended
graphitic crystalline structure oriented along the fibre
axis. However the extension of the graphitic layer
structures normal to the fibre axis is constrained by the
geometric size of the fibres. Interfibre porosity is
present in ThermalGraph[R]. A further disadvantage is that the
high thermal conductivity can only be achieved in one
direction due to the unidirectional orientation of the
fibrous components. Bidirectional properties are difficult
to achieve by simply aligning the fibres in two directions
because of the circular geometry of the fibres.

Mesophase pitch-based carbon fibres may have different
transverse textures which are evident under a scanning
electron microscope. Schematic drawings of the transverse
textures commonly found in circular mesophase pitch-based
carbon fibres are shown in Figure 2. The radial structure
is the most commonly found transverse texture. It is
believed that the transverse texture is "set in" during the
extrusion of mesophase pitch through the spinneret and is
preserved by stabilisation. There have been many attempts to
produce noncircular fibres such as C-shaped, trilobal and
rectangular ribbons. The desire to produce non-circular
carbon fibres is driven by the readiness for stabilisation
of such fibres (compared with round fibres with equivalent
cross-sectional area) because non-circular fibres can have
shorter oxygen diffusion distance from the surface. In
addition, they tend to have better mechanical properties.
However, cross-sectional areas of these fibres are still
relatively small and the subject has been hindered by an
insufficient understanding of microstructural control and
numerous technical problems [Edie *et al*, *Carbon*, 1994, **32**,
1045; Edie *et al*, *Carbon*, 1993, 31, 941; Robinson *et al*,

Carbon, 1996, **34**, 13; Edie *et al*, *High Temperatures-High Pressures*, 1990, **22**, 289; Mochida *et al*, *J. Mater. Sci.*, 1993, **28**, 2331; and Stoner *et al*, *High Temperatures-High Pressures*, 1990, **22**, 299].

Ribbon fibres can be beneficial for making a bidirectional arrangement and are suitable for thermal management applications due to their structure which has high thermal conductivity compared with circular fibres. However known ribbon fibres have small transverse areas and the layer structures which allow graphite growth are constrained. Ribbon fibres developed by Edie *et al* and Mochida *et al* (supra) have small cross-sectional areas. Although different transverse textures are known for circular mesophase pitch-based carbon fibres (radial, onion-skin, flat-layer, radial-folded and random - see Figure 2), only line-origin texture has been reported for ribbon fibres. Edie *et al* used slot dies to produce ribbon fibres (see Figure 2). The largest aspect ratio adopted was 9.

The present invention is based on the recognition that when the aspect ratio of the die slot is increased above conventional levels, the molecular orientation in the extruded and drawn tape undergoes a transition that is a function of shear rate. The invention represents an efficient method for producing carbon materials for *inter alia* thermal management applications and potentially has enormous commercial value.

Thus viewed from one aspect the present invention provides a method for preparing mesophase pitch-based tape comprising: extruding mesophase pitch through a slot shaped die (*eg* a

rectangular die) with an aspect ratio of 10 or more and
drawing at a draw ratio greater than 5.

The method of the invention permits preparation of wider
tapes (or sheets) having enhanced properties in directions
parallel to the plane and over a wider area. Conventional
fibre structures may be replaced with tapes (or sheets) of
the invention in the manufacture of polymer matrix
composites or carbon matrix composites or metal matrix
composites.

In a preferred embodiment of the method of the invention,
the mesophase pitch-based tape is subjected to an elevated
temperature. For example, the mesophase pitch-based tape may
be carbonised to carbon tape or graphitised to graphite
tape.

Preferably the mesophase pitch-based tape is stabilised in a
stabilisation step (eg oxidatively stabilised). Particularly
preferably, stabilisation is followed by heat treatment at
an elevated temperature (eg at a temperature above 400°C).

Preferably the aspect ratio of the die is 20 or more,
particularly preferably 30 or more, more preferably 40 or
more, more especially preferably about 50 or more, even more
especially preferably 60 or more, yet even more especially
preferably 70 or more (eg about 80).

By carefully controlling the shear rate and draw ratio,
mesophase pitch-based tape may be produced in which the
planar molecules predominantly arrange either parallel to
the major tape surface or perpendicular to the major tape
surface. For a die of aspect ratio greater than 10, a lower

shear rate is generally required to produce a tape in which
the planar molecules arrange mainly parallel to the major
tape surface. Conversely, a higher shear rate in the die is
generally required to produce a tape in which the planar
molecules arrange mainly perpendicular to the major tape
surface.

The term shear rate as used herein is defined as:

$$\text{Shear rate at the wall} = (4Q)/(\pi r^3)$$

(where Q is the volumetric flow rate and r is the hydraulic
radius which for a slot-shaped die = 2(area)/perimeter).

Typically the shear rate in the die is in the range 1700 to
$33000s^{-1}$. Preferably the shear rate in the die is in the
range 1700 to $5000s^{-1}$. Preferably the shear rate in the die
is in the range 5000 to $33000s^{-1}$.

For example, for a given mesophase pitch (eg ARA 24) using a
die of aspect ratio 50, a tape in which the planar molecules
arrange mainly parallel to the major tape surface may be
produced using a shear rate in the range 1900 to $4000s^{-1}$ (for
example $1961s^{-1}$, $2017s^{-1}$, $2178s^{-1}$, $2338s^{-1}$, $2599s^{-1}$, $2684s^{-1}$,
$3150s^{-1}$, $3273s^{-1}$, $3363s^{-1}$ or $3830s^{-1}$). For the same mesophase
pitch using a die of aspect ratio 50, a tape in which the
planar molecules arrange mainly perpendicular to the major
tape surface may be produced using a shear rate in the range
5400 to $11100s^{-1}$ (for example $5405s^{-1}$, $5463s^{-1}$, $8053s^{-1}$, $8828s^{-1}$, $8881s^{-1}$, $9126s^{-1}$, $9864s^{-1}$, $10953s^{-1}$, $11084s^{-1}$ or $32921s^{-1}$). For
the same mesophase pitch using a die of aspect ratio 80, a
tape in which the planar molecules arrange mainly parallel
to the major tape surface may be produced using a shear rate

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in the range 1700 to $4900s^{-1}$ (for example $1758s^{-1}$, $2688s^{-1}$, $3189s^{-1}$ or $4828s^{-1}$). For the same mesophase pitch, using a die of aspect ratio 80, a tape in which the planar molecules arrange mainly perpendicular to the major tape surface may be produced using a shear rate in the range 6600 to $12600s^{-1}$ (for example $6617s^{-1}$, $6991s^{-1}$ or $12585s^{-1}$).

By way of example, a die with an aspect ratio of 50 has been used to produce highly oriented continuous mesophase pitch-based tapes which have novel flat-layer transverse texture and a cross-sectional area about 100 times greater than conventional mesophase pitch-based carbon fibres. In addition, the tape maintains excellent mechanical properties. The tensile strength of the carbonised mesophase pitch-based tape with a cross-sectional area of $5000(\mu m)^2$ is of the order of 1GPa. This transverse area is equivalent to that of a circular fibre with a diameter of $80\mu m$. Such a circular fibre would take several days to stabilise and once carbonised would only have a tensile strength of the order of 0.2GPa due to the presence of defects. The electrical resistivity of 2700°C heat-treated mesophase pitch-based tape with cross-sectional area $\sim8000(\mu m)^2$ is $\sim1.2\mu\Omega m$. This is equivalent to that of the most thermally conductive known mesophase pitch-based carbon fibres K1100 which have been heat treated to >3000°C. This suggests that the novel mesophase pitch-based tape of the invention may have lower electrical resistivity when heat-treated to >3000°C. The measured electrical resistivity indicates that high thermal conductivity is expected in accordance with Lavin *et al*, *Carbon*, 1993, **31**, 1001 (see Figure 3).

Viewed from a further aspect the present invention provides a mesophase pitch-based tape (or sheet) obtainable by

extruding mesophase pitch through a slot-shaped die with an aspect ratio of 10 or more, preferably 20 or more, particularly preferably 30 or more, more preferably 40 or more, more especially preferably about 50 or more, even more especially preferably 60 or more, yet even more especially preferably 70 or more (eg about 80). The draw ratio should be greater than 5.

The mesophase pitch-based tape of the invention can have novel orientation with graphite basal planes parallel to the major surface of the tape. This is beneficial to the development of extended graphitic plane structure. The tape may have two-dimensional graphitic properties due to the extended layer structure.

Preferably the mesophase pitch-based tape comprises a flat layer transverse texture.

Preferably the mesophase pitch-based tape comprises graphite basal planes parallel to the major surface of the tape.

In a preferred embodiment, the mesophase pitch based tape of the invention has an extended planar graphitic structure.

In a preferred embodiment, the tape is wound to make pipes or bars.

In a preferred embodiment, the tape is laminated with one or more ceramic materials as interlayers to give oxidation resistance at high temperatures.

In a preferred embodiment, the tape is formed into a honeycomb structure.

In a preferred embodiment, the tape or sheet of flat-layer transverse texture is laminated with fibre, ribbon, tape or sheet of line-origin transverse texture or any other material to control the thermomechanical properties, transport properties and resistance to oxidation.

In a preferred embodiment, the mesophase pitch-based tape is mixed with stabilised tapes from oxidation resistant material [see for example: Lu et al, *Journal of Mater Sci*, **34**, 571-578, 1999] to produce oxidation resistant bulk carbon material.

Viewed from a yet further aspect the present invention provides a process for preparing bulk carbon material, said process comprising:
processing a mesophase pitch-based tape as hereinbefore defined.

The process advantageously comprises the additional step of carbonising to carbonised bulk material or graphitising to graphitised bulk material.

In a preferred embodiment of the process of the invention, the processing step comprises: laminating or pressing the mesophase pitch-based tape.

Pressing is preferred and may be conducted at a carefully chosen pressures for a suitable length of time. By controlling the pressure used during pressing, it is possible to produce a range of bulk carbon materials with different thermal and mechanical properties. Typically pressing may be carried out a pressure of about 15-35MPa at

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an elevated temperature (eg about 400°C) for an extended period of time (eg about 2 hours).

Preferably, the mesophase pitch-based tapes are stabilised (eg oxidatively stabilised) prior to pressing.

The process of the invention produces a high density bulk carbon material without any need for liquid phase impregnation or vapour phase infiltration.

Viewed from a further aspect the present invention provides a bulk carbon material obtainable by processing a mesophase pitch-based tape as hereinbefore defined.

In accordance with the invention, the highly oriented mesophase pitch-based graphite (HOMG) tapes and the bulk HOMG carbon materials have superior properties due to the two-dimensional extensive planar graphitic structure of the tapes and higher density of the final bulk product. Due to the high degree of orientation of the mesophase pitch-based tape, the bulk carbon (eg graphite material) is expected to have excellent transport properties.

The bulk carbon materials of the invention can be utilised in the aerospace, nuclear, metallurgical, chemical, mechanical, electronic and electrical industry. In particular, they are best suited in areas where heat generation limits efficiency or leads to component failure such as in high power electronic devices, high energy friction and braking systems, propulsion and energy generation equipment, as well as processing equipment operating in corrosive environments. The low production costs of the method and process of the invention will assist

widespread applications in these thermal management areas. Manufacturers will benefit from cheaper production cost and high performance products and user will benefit from improved devices with greater thermal properties and reliability.

The invention has been and will now be described in a non-limitative sense with reference to the Example and the accompanying Figures in which:

Figure 1: Schematic illustration of mesophase spheres coalescing to a larger sphere;

Figure 2: Schematic illustration of the transverse textures of various pitch-based carbon fibres (a) radial (b) onion skin (c) random (d) flat layer (e) line-origin ribbon fibre;

Figure 3: Relationship between electrical resistivity and thermal conductivity of mesophase pitch-based carbon fibres (Lavin et al, Carbon, 1993, 31, 1001);

Figure 4: A flow diagram representing the route to graphite tape and its bulk material;

Figure 5: Texture of typical carbon tape; and

Figure 6: Schematic illustrations of bulk carbon material from tapes and circular fibres.

Example 1

An embodiment of the method of the invention for producing mesophase pitch-based tapes is outlined schematically in Figure 4. A commercial mesophase pitch ARA24 (100% anisotropic content, softening point 237°C) was used to prepare pitch tapes. The spinning precursor was formed into tape by a bench-scale melt-extrusion system at a temperature of 290°C through slit-shaped dies and drawing the extrudate.

The molten mesophase pitch was forced through the die by
nitrogen gas. Three dies were used with rectangular slot
dimensions of 0.14mm x 2.4mm, 0.1mm x 5 mm, and 0.1 mm x 8mm
respectively. The depth of the slot is 0.5mm. Upon exiting
the slot dies, the tapes were draw down and collected under
ambient conditions on a variable speed winder. The draw
ratio is defined as the thickness of the slot (eg 0.14 mm or
0.1 mm) divided by the thickness of the as-spun pitch tape
prior to further treatment. The cross-sectional area of the
tape was varied with the aspect ratio of the dies, shear
rate and winding speed.

The mesophase pitch-based tape was produced using a die of
aspect ratio 50 at a shear rate of $2338s^{-1}$ (spinning
temperature 290°C, pressure 8 bar). The shear rate in the
slot die is defined as the product of four times the volume
flow rate (cm^3/sec) divided by the product of π times the
cube of the hydraulic radius (cm) of the slot die. The
hydraulic radius of the slot die is defined as the product
of two times the cross-sectional area of the slot die (cm^2)
divided by the perimeter of the slot die (cm).

The as-spun tape was oxidatively stabilised in air or oxygen
at a temperature below 300°C producing a weight gain of 8-10%
and then carbonised at 1000°C under nitrogen atmosphere. Some
carbon tapes were further heat-treated at a higher
temperature eg 2700°C.

The parallel sheet-like texture of carbon tapes is evident
under the optical microscope and scanning electron
microscope. This texture has been confirmed by results of X-
ray diffraction (XRD) texture scan. The 1000°C heat-treated
carbon tape is highly flexible with a transverse area

comparable to a combined transverse area of 100-200 conventional mesophase pitch-based carbon fibres. The carbon tape can be coiled into a sample vial with internal diameter of 20 mm. This carbon tape is also strong with a tensile strength of the order of 1GPa. After graphitisation at 2700°C, it shows unusual fracture behaviour with evidence of progressive failure and sliding of layers. Together with the highly irregular and fibrillar tensile fracture surface, this indicates that the tape has significant fracture toughness. This is believed to be due to the predominantly planar orientation of the structure combined with limited regions of locally misoriented structure that deflect the crack path and so hinder crack propagation. The ultimate strength was around 2GPa and the initial Young modulus is of the order of 500GPa.

The HOMG tape (HTT 2700°C) has an average electrical resistivity of $1.2\mu\Omega m$ equivalent to the value of K1100 that has been heat treated at a much higher temperature (>3000°C). This suggests that the HOMG tape can have a thermal conductivity value equivalent to K1100 if the inverse relationship between electrical resistivity and thermal conductivity for mesophase pitch-based carbon fibres is still valid for carbon tape (Fig. 3). The Raman spectrum and XRD profile demonstrate the highly graphitic structure of the HOMG tape.

Example 2

For the same mesophase pitch, using a die of aspect ratio 50 and a shear rate of eg $1961s^{-1}$, $2017s^{-1}$, $2178s^{-1}$, $2599s^{-1}$, $2684s^{-1}$, $3150s^{-1}$, $3273s^{-1}$, $3363s^{-1}$ or $3830s^{-1}$, tapes in which

the planar molecules arrange predominantly parallel to the
major tape surface were produced.

Example 3

For the same mesophase pitch, using a die of aspect ratio
50, and a shear rate in the die of *eg* 5405s^{-1}, 5463s^{-1}, 8053s^{-1}, 8828s^{-1}, 8881s^{-1}, 9126s^{-1}, 9864s^{-1}, 10953s^{-1}, 11084s^{-1} or
32921s^{-1}, tapes in which the planar molecules arrange
predominantly perpendicular to the major tape surface were
produced.

Example 4

For the same mesophase pitch, using a die of aspect ratio 80
and a shear rate of *eg* 1758s^{-1}, 2688s^{-1}, 3189s^{-1}, 4828s^{-1}, tapes
in which the planar molecules arrange mainly parallel to the
major tape surface were produced.

Example 5

For the same mesophase pitch, using a die of aspect ratio 80
and a shear rate of *eg* 6617s^{-1}, 6991s^{-1} or 12585s^{-1}, tapes in
which the planar molecules arrange mainly perpendicular to
the major tape surface were produced.

Example 6

Mesophase pitch was melt extruded from a rectangular die
with an aspect ratio of 50 and continuously wound on to
carbon felt which was fastened on a roller. The as-spun
tapes were oxidatively stabilised and then cut into desired
length. The tapes were loaded into a rectangular mould along

one direction and compacted under hot press with a ram
pressure of 5-10 ton at a temperature of 400°C for 2 hours
(see Fig. 6). These tapes softened under the effect of
pressure and temperature and fuse together. However, the
preferred orientation induced during extrusion and winding
was retained. The bulk material was removed from the mould
and heat treated under inert atmosphere to convert it into
bulk carbon material.

For comparison, a circular fibre was used to make a similar
bulk material. A schematic diagram of the various materials
is shown in Figure 6. After carbonisation, the bulk carbon
material from circular fibres cracked into a few pieces.
However the bulk carbon material from a tape of the
invention maintained integrity with no obvious cracks
developed on the surfaces. This is attributable to the
circular fibre structural constraints which inhibit
shrinkage while the parallel nature of the layer planes in
the tapes allows shrinkage and dissipation of such stresses.

The advantage of pressing stabilised tapes into desired
shape is that the size of bulk materials is not limited by
the subsequent stabilisation process as in Amoco's method.
Additionally the tapes may be pressed at higher pressure to
achieve higher bulk density of the order of 1.8 Mgm^{-3}. For
example, after carbonisation at 1000°C, the bulk carbon
material has an apparent density of the order of 1.9 Mgm^{-3}
and the tapes are closely bonded together with little inter-
tape porosity. The bulk carbon material has preferred
orientation of layer structure parallel to the main bulk
carbon surface. The pressure used for formation of the bulk
materials must be carefully controlled so as not to destroy
the individual tape to ensure high strength of the bulk

material. The bulk carbon materials obtained from tapes have higher density than those from circular fibres due to the lower porosity. This leads to a self-reinforced carbon material with two-dimensional ultra-high thermal conductivity at considerably reduced production cost.